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(19) (CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) **Metallocenes Containing Aryl-Substituted Indenyl Derivatives as Ligands, Process for Their Preparation, and Their Use as Catalysts**

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(57) 12 Claims

Notice: This application is as filed and may therefore contain an incomplete specification.

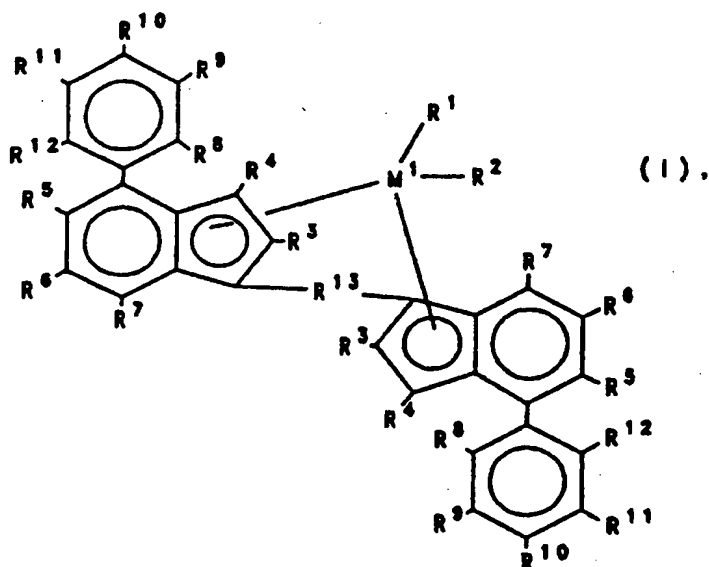
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Abstract of the disclosure

Metallocenes containing aryl-substituted indenyl derivatives as ligands, process for their preparation, and their use as catalysts.

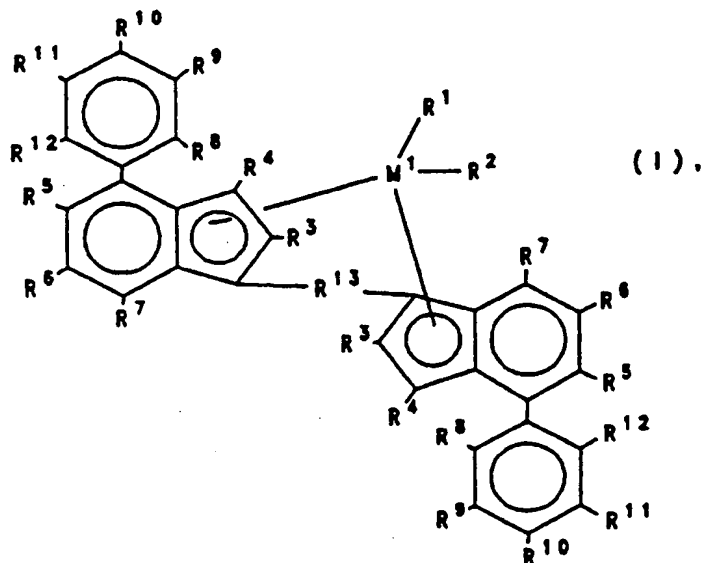
A very effective catalyst system for the polymerization or copolymerization of olefins comprises a cocatalyst, preferably an aluminoxane or a supported aluminoxane, and a metallocene of the formula I



in which, in the preferred form, M^1 is Zr or Hf, R^1 and R^2 are halogen or alkyl, R^3 is alkyl, R^4 to R^{12} are alkyl or hydrogen and R^{13} is a (substituted) alkylene or heteroatom bridge. The metallocenes, in particular the zirconocenes, produce polymers of very high molecular weight, in the case of prochiral monomers polymers of very high molecular weight, very high stereotacticity and very high melting point, at high catalyst activities in the industrially particularly interesting temperature range between 50 and 80°C. In addition, reactor deposits are avoided by means of supported catalyst systems.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A compound of formula I



in which

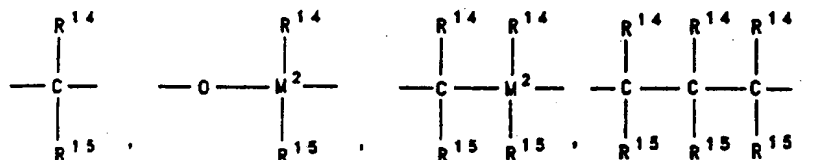
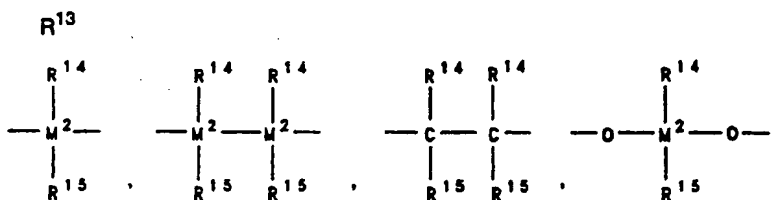
M^1 is a metal from group IVb, Vb or VIb of the Periodic Table,

R^1 and R^2 are identical or different and are a hydrogen atom, a C_1 - C_{10} -alkyl group, a C_1 - C_{10} -alkoxy group, a C_6 - C_{10} -aryl group, a C_6 - C_{10} -aryloxy group, a C_2 - C_{10} -alkenyl group, a C_7 - C_{40} -arylalkyl group, a C_7 - C_{40} -alkylaryl group, a C_6 - C_{40} -arylalkenyl group, an OH group or a halogen atom,

the radicals R^3 are identical or different and are a hydrogen atom, a halogen atom, a C_1 - C_{10} -alkyl group, which may be halogenated, a C_6 - C_{10} -aryl group, an $-NR^{16}_2$, $-SR^{16}$, $-OSiR^{16}$, $-SiR^{16}$, or $-PR^{16}_2$ radical, in which R^{16} is a halogen atom, a C_1 - C_{10} -alkyl group or a C_6 - C_{10} -aryl group,

R^4 to R^{12} are identical or different and are as defined for R^3 , or adjacent radicals R^4 to R^{12} , together with the atoms connecting them, form one or more aromatic or aliphatic rings, or the radicals R^5 and R^8 or R^{12} , together with the atoms connecting

them, form an aromatic or aliphatic ring,
 R^{13} is



- 5 $=BR^{14}$, $=AIR^{14}$, $-\text{Ge}-$, $-\text{O}-$, $-\text{S}-$, $=\text{SO}$, $=\text{SO}_2$, $=\text{NR}^{14}$, $=\text{CO}$,
 $=\text{PR}^{14}$ or $=\text{P}(\text{O})\text{R}^{14}$, where R^{14} and R^{15} are identical or
different and are a hydrogen atom, a halogen atom,
a C_1 - C_{10} -alkyl group, a C_1 - C_{10} -fluoroalkyl group, a
 C_1 - C_{10} -alkoxy group, a C_6 - C_{10} -aryl group, a
10 C_6 - C_{10} -fluoroaryl group, a C_6 - C_{10} -aryloxy group, a
 C_2 - C_{10} -alkenyl group, a C_7 - C_{40} -arylalkyl group, a
 C_7 - C_{40} -alkylaryl group or a C_8 - C_{40} -arylalkenyl group,
or R^{14} and R^{15} , in each case together with atoms
connecting them, form one or more rings, and
15 M^2 is silicon, germanium or tin.

2. A compound of the formula I as claimed in claim 1,
wherein, in the formula I,
 M^1 is zirconium or hafnium,

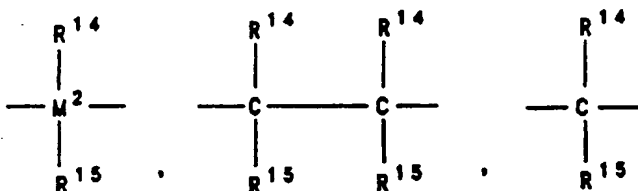
R^1 and R^2 are identical and are a C_1 - C_3 -alkyl group
or a halogen atom,

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the radicals R^3 are identical and are a C_1 - C_4 -alkyl
group

R^4 to R^{12} are identical or different and are hydrogen or a C_1 - C_4 -alkyl group, and

R^{13} is



5 where M^2 is silicon or germanium and R^{14} and R^{15} are identical or different and are a C_1 - C_4 -alkyl group or a C_6 - C_{10} -aryl group.

3. A compound of the formula I as claimed in claim 1, wherein, in the formula I,

10 R^4 and R^7 are hydrogen, and

R^5 , R^6 and R^8 to R^{12} are identical or different and are hydrogen or a C_1 - C_4 -alkyl group.

4. A compound of the formula I as claimed in claim 1, wherein, in formula I,

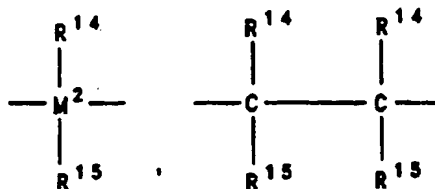
15 M^1 is zirconium,

R^1 and R^2 are identical and are chlorine, the radicals R^3 are identical and are a C_1 - C_4 -alkyl group,

R^4 and R^7 are hydrogen,

20 R^5 , R^6 and R^8 to R^{12} are identical or different and are a C_1 - C_4 -alkyl group or hydrogen, and

R¹³ is



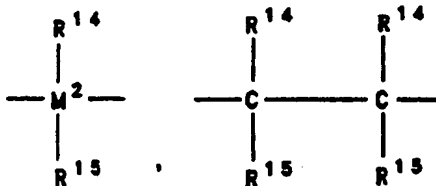
where M² is silicon and R¹⁴ and R¹⁵ are identical or different and are a C₁-C₄-alkyl group or a C₆-C₁₀-aryl group.

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5. A compound of formula I as claimed in one or more of claims 1 to 4, wherein, in the formula I,

M¹ is zirconium, R¹ and R² are chlorine, the radicals R³ are methyl or ethyl, R⁴ to R¹² are hydrogen, and R¹³ is

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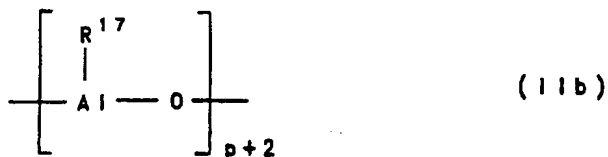
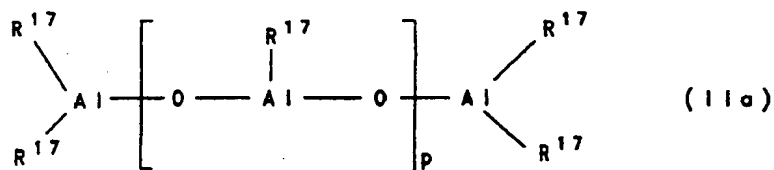


where M² is silicon, and R¹⁴ and R¹⁵ are identical or different and are methyl, ethyl, n-propyl, i-propyl or phenyl.

- 15 6. A process for the preparation of an olefin polymer by polymerization or copolymerization of an olefin of the formula R^a-CH=CH-R^b, in which R^a and R^b are identical or different and are a hydrogen atom or a hydrocarbon radical having 1 to 14 carbon atoms, or
- 20 R^a and R^b, together with the atoms connecting them,

can form one or more rings, and at a temperature of from -60 to 200°C, at a pressure of 0.5 to 100 bar, in solution, in suspension or in the gas phase, in the presence of a catalyst formed from a metallocene as transition-metal compound and a cocatalyst, wherein the metallocene is a compound of the formula I as claimed in claim 1.

7. The process as claimed in claim 6, wherein the cocatalyst used is an aluminoxane of the formula IIa for the linear type and/or of the formula IIb for the cyclic type



- where, in the formulae IIa and IIb, the radicals R¹⁷ are identical or different and are a C₁-C₆-alkyl group, a C₆-C₁₀-aryl group, benzyl or hydrogen, and p is an integer from 2 to 50.

8. The process as claimed in claim 6, wherein the cocatalyst used is methylaluminoxane.
9. The process as claimed in claim 6, wherein the metallocene of the formula I is preactivated by

means of an aluminoxane of the formula IIa and/or IIb before use in the polymerization reaction.

- 5 10. The process as claimed in claim 6, wherein a supported polymerization catalyst is employed which is the product of the reaction of a metallocene of the formula I with a supported organoaluminum compound (cocatalyst).
- 10 11. The process as claimed in claim 10, wherein the support material is an oxide of silicon and/or of aluminum, and the organoaluminum compound is methylaluminoxane.
12. The use of a metallocene of formula I as claimed in claim 1 as a catalyst component in the polymerization or copolymerization of olefins.